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RAPID LINEAR PYROLYSIS OF COMPOSITE SOLID PROPELLANT INGREDIENTS

By Donald R. Simon

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Prepared under Contract No. NAS1-8450
Vitro Laboratories
Silver Spring, Md.

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Langley Research Center
Hampton, Virginia 23365

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ABSTRACT

Polymeric materials have been exposed to high levels of surface heat flux (up to 1,000 cal cm^{-2} sec^{-1}) and the resulting linear regression rates (up to 3 mm sec^{-1}) measured. A novel microthermometry technique was developed to measure the subsurface temperature distributions and applied successfully in obtaining linear pyrolysis characteristics of polymethylmethacrylate. All polymeric materials tested exhibited a liquid layer on the regression surface; and for polymethylmethacrylate it appeared to increase in thickness with increasing surface heating rate (and therefore regression surface regression rate). Although not reported in the earlier literature, it is mentioned frequently in recent publications. No linear pyrolysis model exists that accounts for it directly, but its presence could strongly influence combustion characteristics of systems of practical interest--for example, composite solid propellants.

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I. INTRODUCTION

This study was undertaken for the purpose of developing a better understanding of the response of physical and chemical properties that take place in certain polymeric materials exposed to intense surface heating. This information is required in order to establish a quantitative understanding of the deflagration mechanism of composite solid propellants incorporating these materials. Two simple, commercially available polymeric materials were chosen for this study because of their similarity to typical propellant ingredients and because they have been studied extensively in the past. These materials are polymethylmethacrylate (hereafter abbreviated as PMM) and polyalphamethylstyrene (PAMS). In addition, measurements were made on polyurethane, supplied by the Navy Propellant Plant. This material is the standard reference binder of the Interagency Chemical Rocket Propulsion Group (ICRPG). Finally, for comparison purposes, an ammonium perchlorate-polymethane composite propellant (ICRPG standard reference propellant) was tested as well.

The experimental approach consists of exposing samples to intense levels of surface heat flux, and measuring the surface regression rate and temperature profile beneath the regressing surface. Such data are necessary in order to reveal the true nature of the surface decomposition-vaporization process, at conditions approximating

those encountered at the surface of a propellant burning under typical rocket motor conditions--surface regression rates of several mm/sec, surface temperatures of several hundred ^{o}C, and subsurface temperature gradients of several $^{o}C/\mu m$.

The "classical" bulk decomposition experiments, involving mild heating and low temperatures, yield data that are not germane to the propellant combustion situation.

Test specimens were exposed to the intense, well-controlled thermal flux from an impinging plasma-jet. The jet was produced by a Vitro Fluid Transpiration Arc[1] that operates at power levels up to 80 kW; the plasma plume was shaped and directed onto the sample surface by a water-cooled nozzle. Previously reported studies[2,3] of surface decomposition-vaporization (or linear pyrolysis) of propellant materials have yielded data at regression rates up to about 0.5 mm/sec. The more intense plasma jet heating used here enables us to make measurements at regression rates up to 3.0 mm/sec.

Previous experimenters have used micro-thermocouples embedded in the sample material in an attempt to measure the temperature distribution beneath the regressing surface[2]. At the extreme conditions of the present work, this method is impractical. Thermocouples cannot be made small enough to discern accurately the details of the sharp subsurface gradients. Thus, a novel approach was taken.

It involved embedding very thin opaque films in the bulk material and then measuring the film temperature by detecting its infrared emission. A great deal of effort in this program was devoted to the development of this technique.

II. EXPERIMENTAL METHOD

Thin-film IR Radiometer

A major portion of this program was devoted to adapting for linear pyrolysis studies a thin metallic film temperature sensing technique conceived by Kantrowitz, et. al.[4] The principal reasons for employing this technique, as opposed to the previously employed fine thermocouple[2, 3] technique, under the extreme conditions encountered are the following:

a) Due to its very small dimension (less than 1 μm) in the direction of the temperature gradient, it subtends a negligible temperature difference (see Figure 1).

b) Due to its very small dimension in the direction of the temperature gradient, the film has a very small "thermal inertia," so that it can follow temperature changes with a response time of several microseconds.

c) Due to the fact that the radiant output is detected, which varies as the fourth power of absolute temperature, the sensitivity of the detection system varies approximately with the fourth power of temperature, so the potential for accurate surface temperature is high.

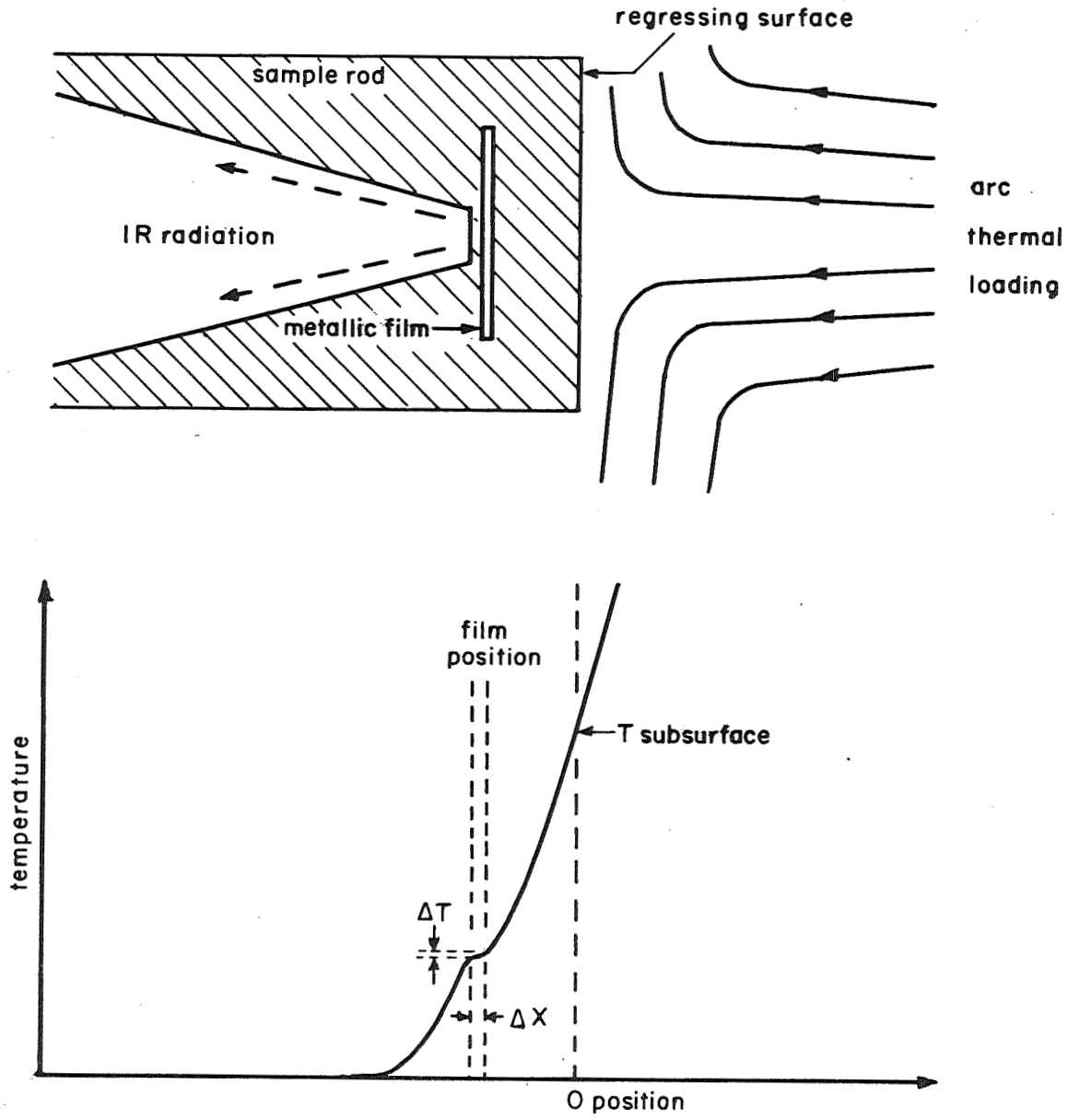

Figure 1. Details of sample and embedded film

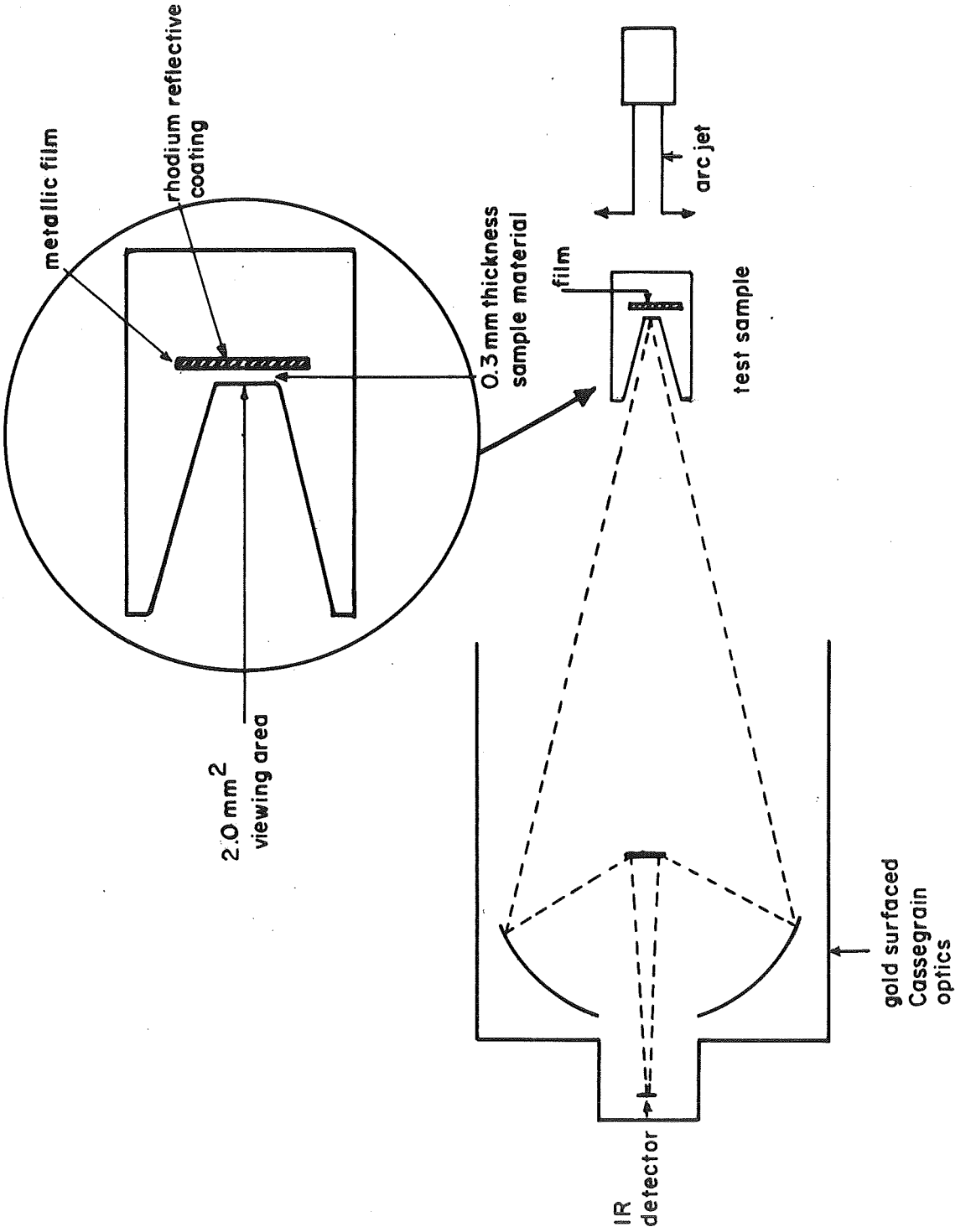

Figure 2. Optical Arrangement

The IR radiometer is shown schematically in Figure 2. A Cassegrainian optical system was employed to focus the IR radiation, in the band between 1.0 μ and 3.0 μ on a 1 x 5 mm lead sulfide cell (Kodak Ektron).

The radiation emanates from the back surface of the film embedded within the sample and situated at the object plane of the optical system. The optical path was surrounded by a series of fixed (A and B) and movable (C) water-cooled baffles which also serve as defining apertures (see Figure 3).

The original carbon film was replaced by a nickel film coated with rhodium to minimize the influence of radiant loading from the arc.

The complete system was statically calibrated in situ by heating the metallic film with a hot plate whose temperature was monitored with a chromel-alumel thermocouple. The experimental calibration points were fitted with a smooth curve as shown in Figure 4.

Preliminary tests had revealed two sources of spurious response in the IR radiometer. The first was electrical: the carbon composition resistors used as load resistors for the lead sulfide cell were excessively noisy. By replacing these with metal-film resistors, the circuit noise was eliminated except for the intrinsic noise in the detector itself. The second was optical: spurious radiant inputs were caused by radiation from the heated gases, and from debris blown from the sample. This problem was eliminated with the use of several water-cooled optical baffles, and a reflective foil liner in the exit cone of the sample.

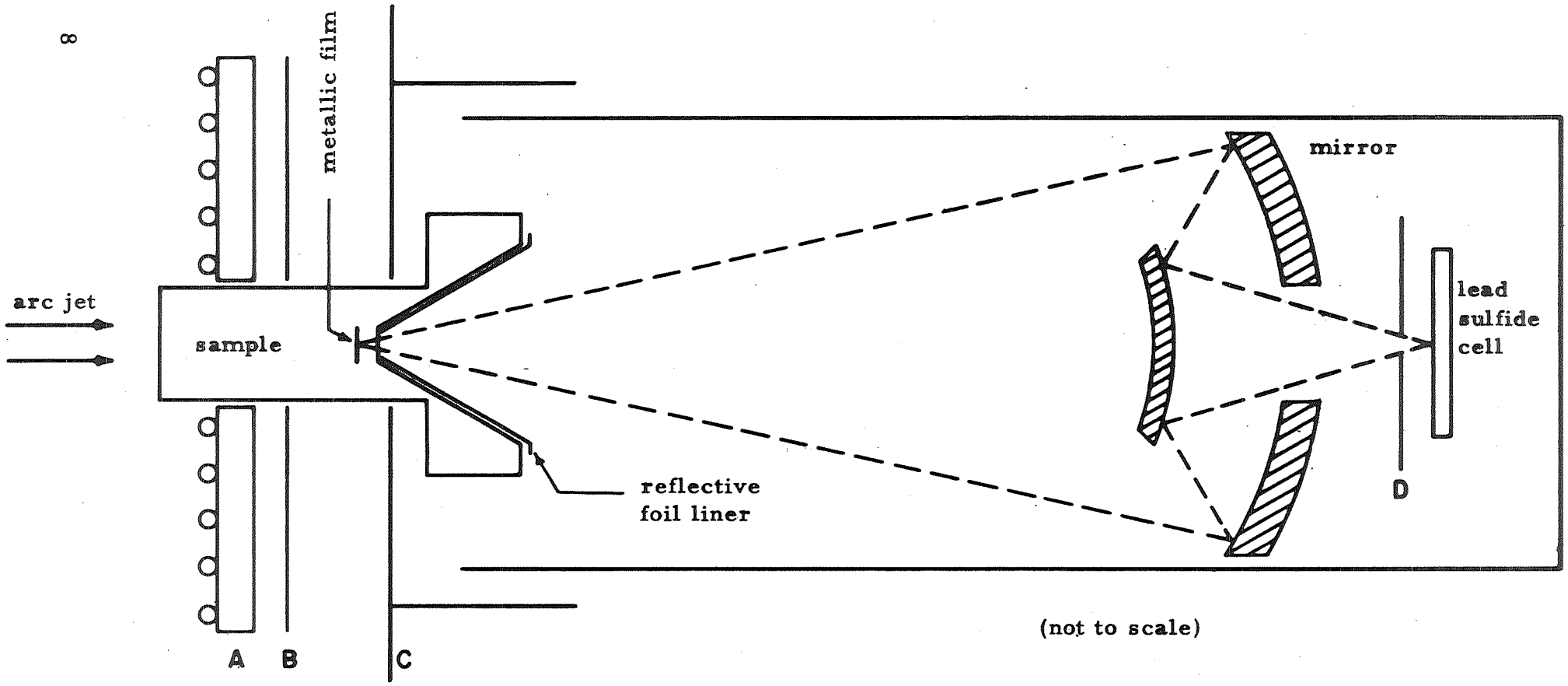

Figure 3. Section view of sample, metallic film, collecting optics, and IR detector (lead sulfide cell). The water-cooled baffle A (fixed) and secondary baffles B and C (movable) were added to prevent circulation of hot gases into the optical path. An additional baffle at D limits the field of view of the optical collector.

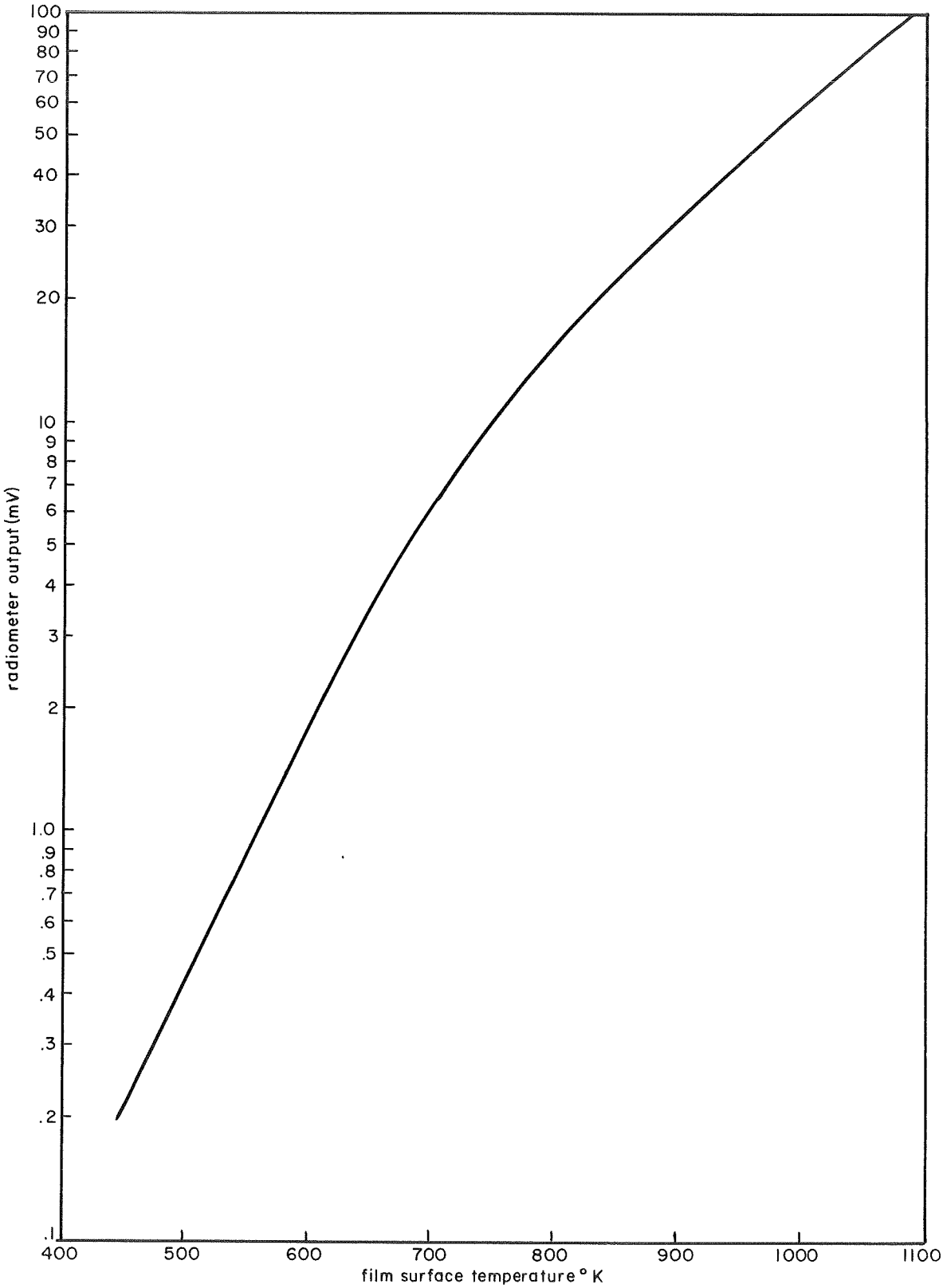

Figure 4. Calibration curve of IR radiometer

Early experiments were performed using a lead sulfide detector having a relatively large sensing area (3 mm x 10 mm) and a high internal impedance (400 kΩ). It was necessary to view a relatively large area of the radiating film in order to get a usable signal-to-noise ratio from the detector. Unfortunately, errors due to misalignment between the film and regressing specimen surface increase with film area viewed, and the mm^2 required for a tolerable signal-to-noise ratio using the first cell was unacceptable. Substitution of a cell with a relatively small viewing area (2 mm^2) (Kodak Ektron) resulted in a factor of 20 noise reduction, and "clean," reproducible signals. A composite of some of this data is shown as Figure 5.

Initially, great difficulty was encountered in mounting the film in the specimens so that there would be intimate contact over the entire area of the film. Eventually, acceptable adhesion was obtained with PMM by using methylethylketone as a solvent and pressing together (during the curing process) the ends of the two cylindrical rods with the film sandwiched between. Unfortunately, time did not allow development of a successful technique for the other materials tested.

Transpiration Calorimeter

A specially designed, transpiration calorimeter was developed to permit determination of the heating characteristics of the impinging jet when there is outgassing from the target surface (Figure 6). The

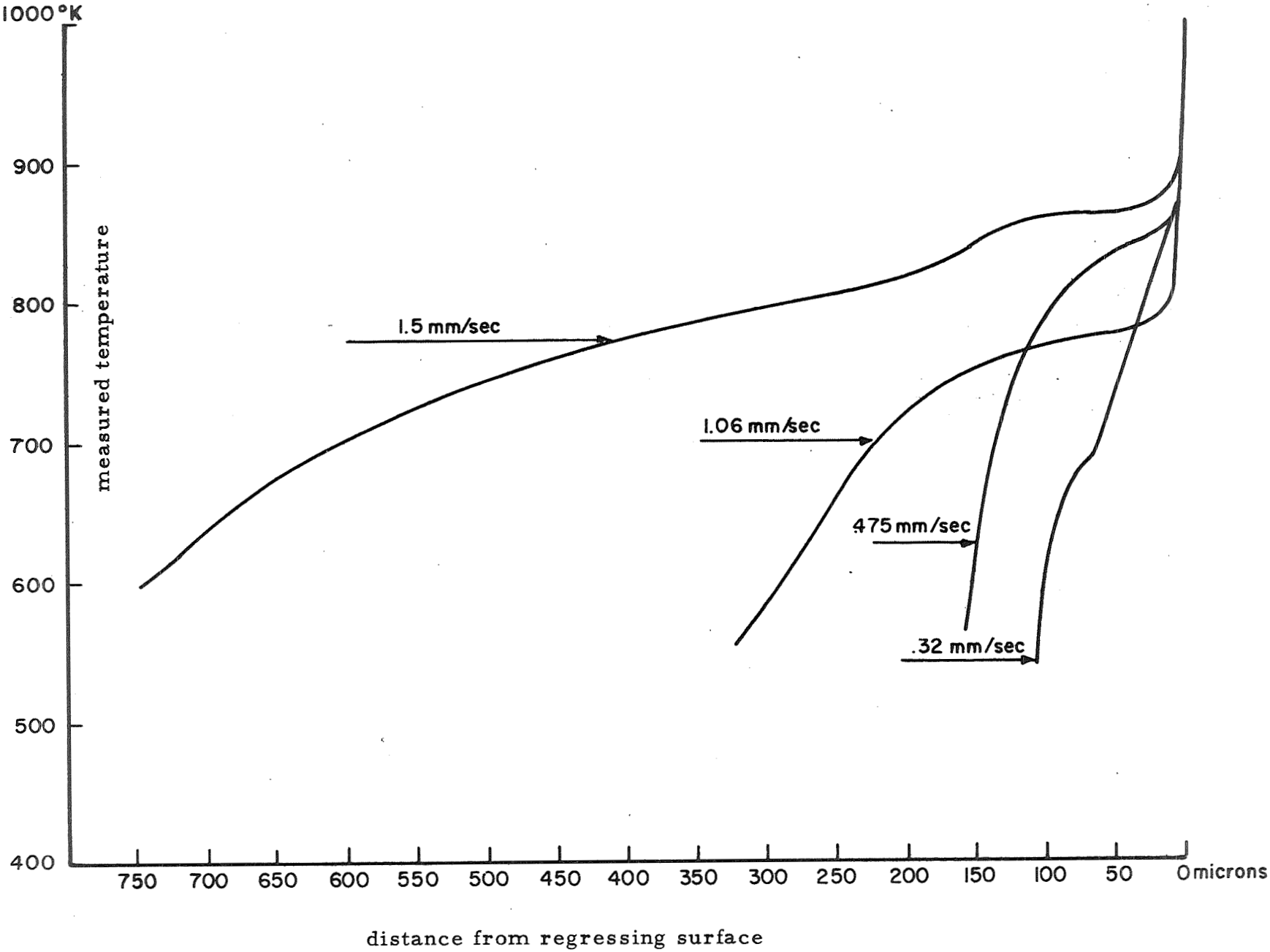

Figure 5. Composite of temperature profiles in PMM. Representative curves at regression rates from 0.32 to 1.5 mm/sec are shown.

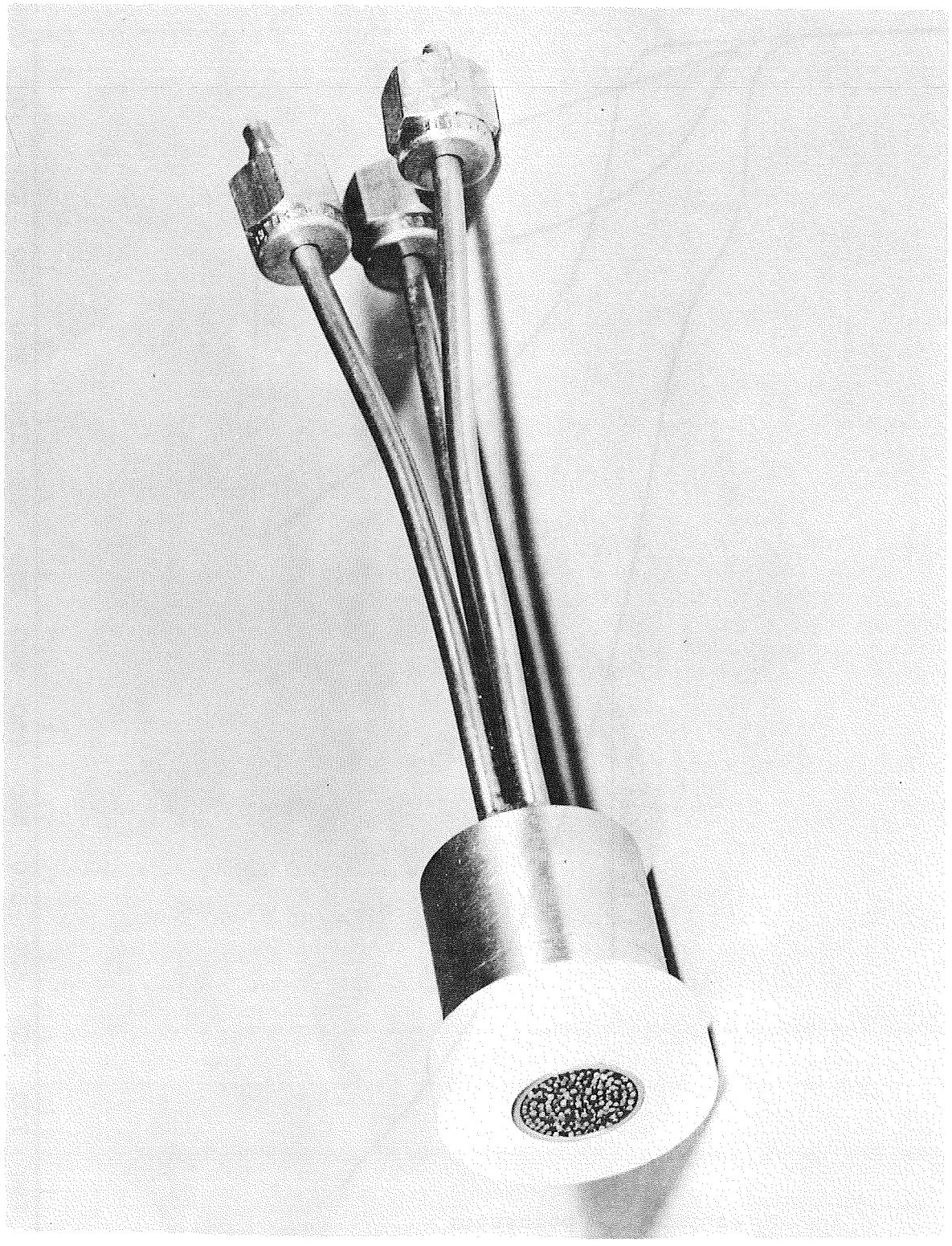

Figure 6. Transpiration calorimeter

porous surface of the calorimeter has the same cross-sectional area of the test specimens. At each of several plasma-jet operating conditions CO_2 was expelled at a mass flow rate corresponding to the previously measured specimen linear pyrolysis rate. In this way it was possible to account experimentally for the heat blockage due to transpiration cooling.

The results of the tests using the transpiration probe to determine the insulating effect of blow-off gas were surprising. By comparing the heat input to the porous tungsten surface with and without a gas flow, we were able to determine that the evolving gas blocked somewhat less than 10% of the cold-wall thermal loading - a smaller effect than expected. The mass flow rate of gas was chosen equal to the evolution rate from a PMM sample at the same loading. Carbon dioxide was used because it is a major constituent of degrading PMM at high temperature. It is interesting to note that the mass flow rate from the evolving gases was only 0.1% of the impinging arc flow, and yet it had the effect of reducing the loading by about 10%.

Satisfactory film mounting techniques for the PAMS and ICRPG specimens could not be developed in the interval between the successful development of the technique for the PMM and the program termination. Therefore, temperature data could not be obtained for these materials.

Exposure of ICRPG specimens to high heating rates resulted in extensive melting--so much, in fact, that it was impossible to determine the actual mass vaporization rate because of the droplets blown from the surface. At lower levels of exposure, where the degree of melting was reduced, the regression rate appeared to be about twice that of PMM (e.g., $r \approx 1.4$ mm/sec when $q \approx 120$ cal/cm^2 sec).

A few experiments were made to assess the dependence of ICRPG propellant burning rate to exposure to thermal radiation. The radiation emerging from the fluid transpiration arc was imaged on the propellant surface. Ignition was achieved by thermal irradiation from the source.

III. EXPERIMENTAL RESULTS

The subsurface temperature profiles of PMM were measured using the embedded thin film technique at regression rates between 0.3 mm/sec and 1.5 mm/sec. Unfortunately, after successful development of the technique, only a limited number (9) of successful runs could be made before termination of the program. However, time did not allow taking of sufficient data to establish reproducibility levels.

An oscillograph of the IR detector output history for a PMM sample subjected to a heating load at 50 cal/cm^2-sec is shown in Figure 7. The abrupt change in signal level is interpreted as the breakout of the thin film into the surrounding high temperature gaseous region. Other runs did not exhibit such a clearly defined characteristic. Thus, there was uncertainty in establishing the condensed phase/vapor phase interface temperature. This is reflected by means of the error brackets in the data displayed in Figure 8. Figure 9 is a semi-log plot of regression rate versus reciprocal absolute surface temperature. Also displayed are data from Reference 2.

The existence of a liquid layer at the regressing surface was indicated by visually observing the regressing surface during a run, and confirmed by plunging a blunt rod (1 mm diameter) into the surface immediately after interrupting heating (Figure 10). Other experimenters

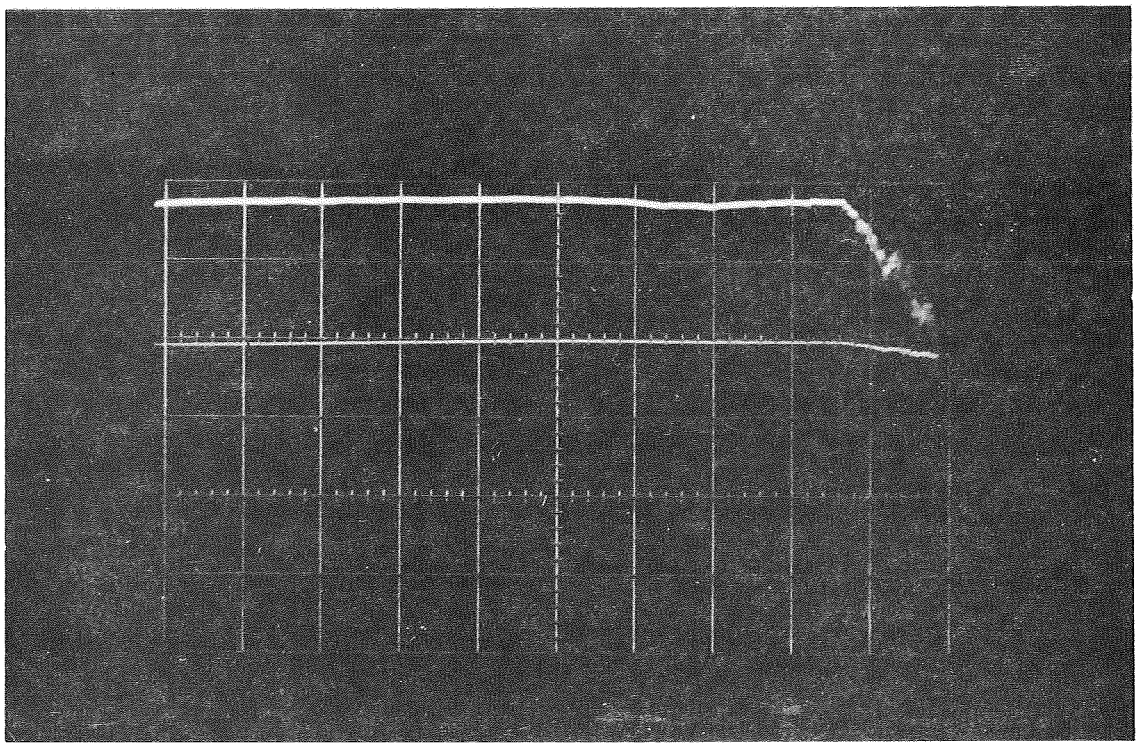

Figure 7. Output signal from IR detector vs time. Output is negative-going signal displayed at 50 mV/div in upper trace; same signal at 500 mV/div in lower trace. Time scale is 0.2 sec/div. Breakthrough occurs at 90 mV or 825° K. Sensitivity is about 2 mV/°K at this temperature. Regression rate is 0.65 mm/sec. Sample is PMM.

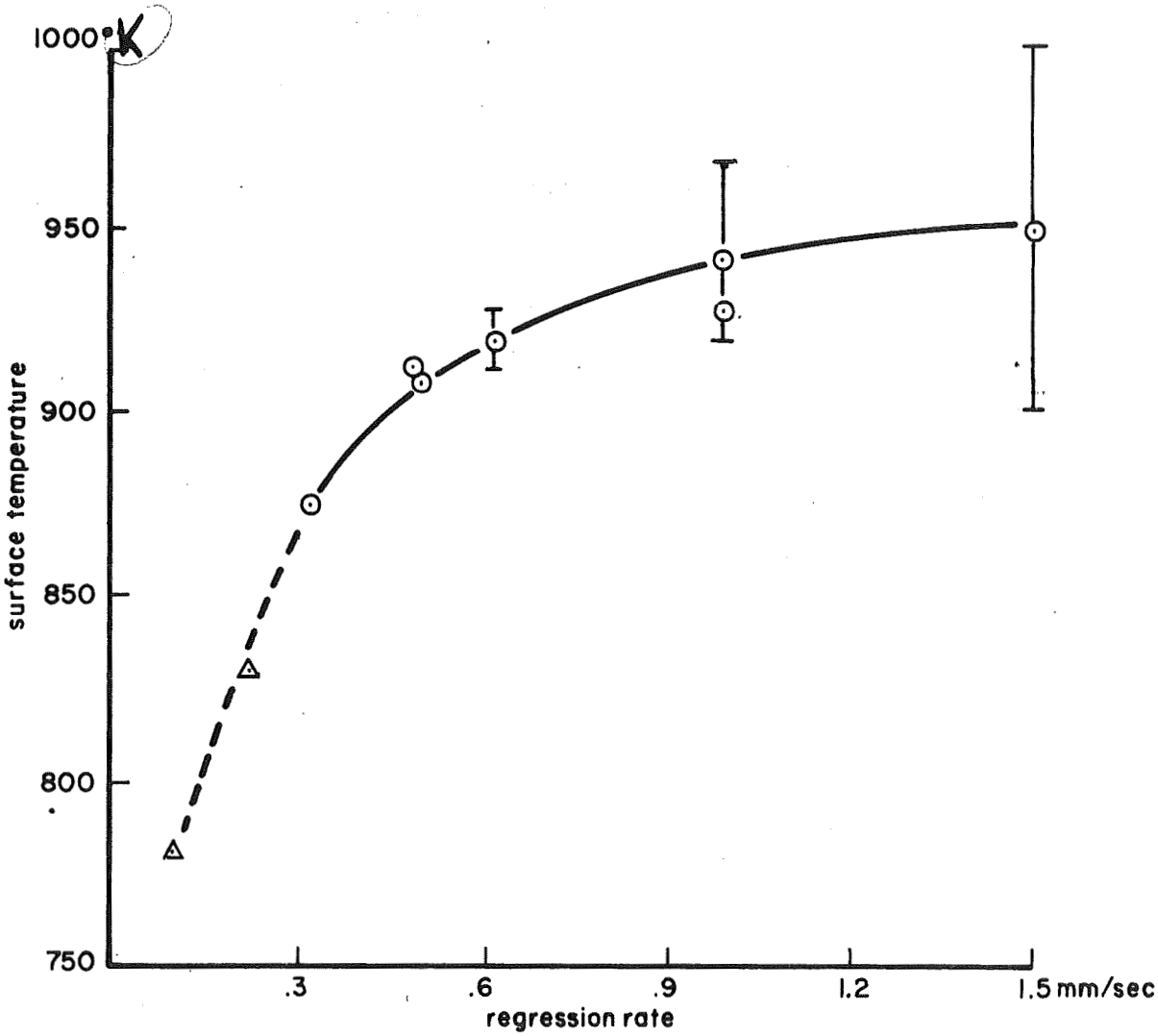

Figure 8. Surface temperature vs regression rate for PMM.

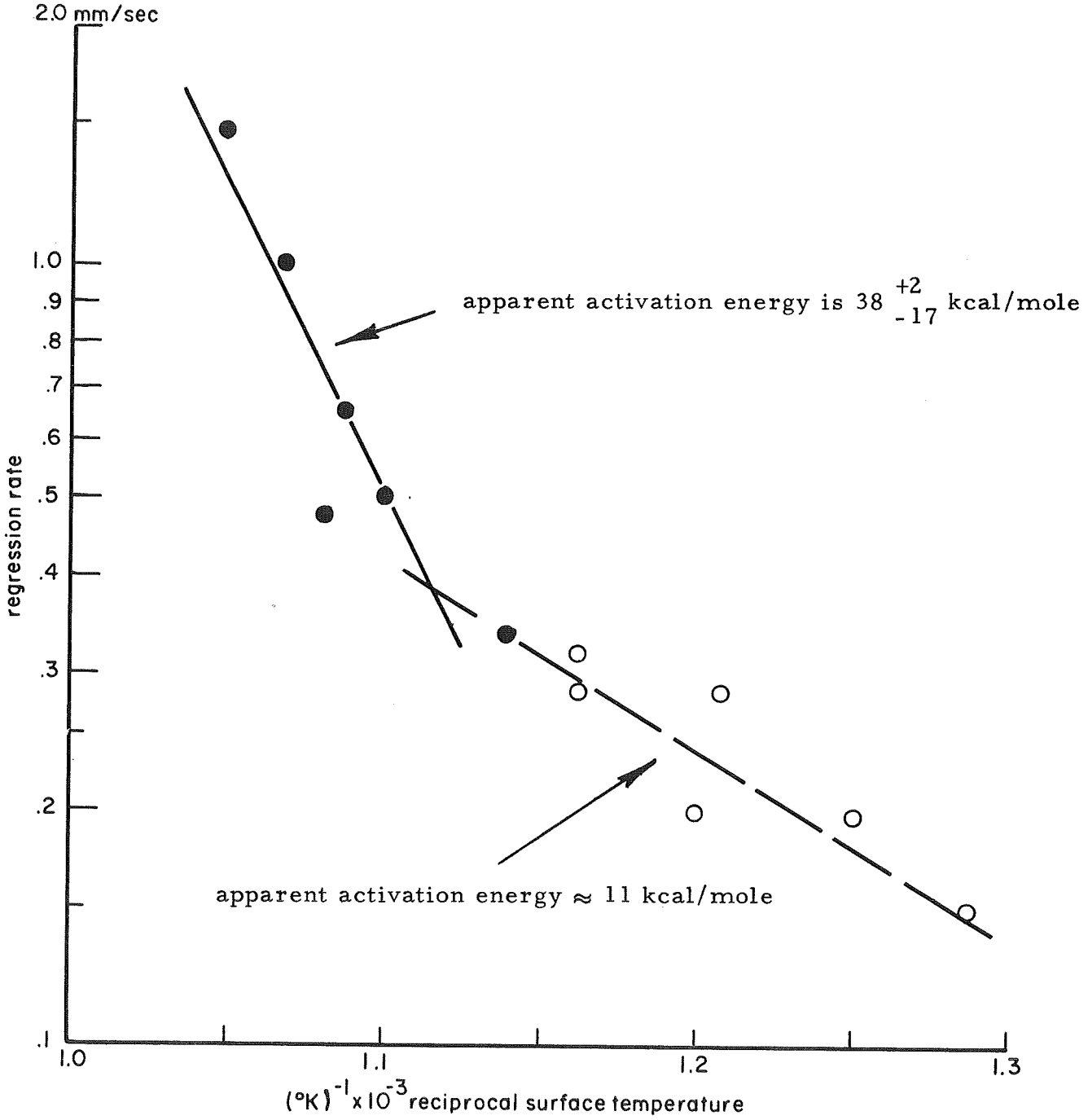

Figure 9. Regression rate vs reciprocal surface temperature for PMM. Data from this experiment shown as solid dots. Data from McAlevy, et. al.[2] shown as open circles.

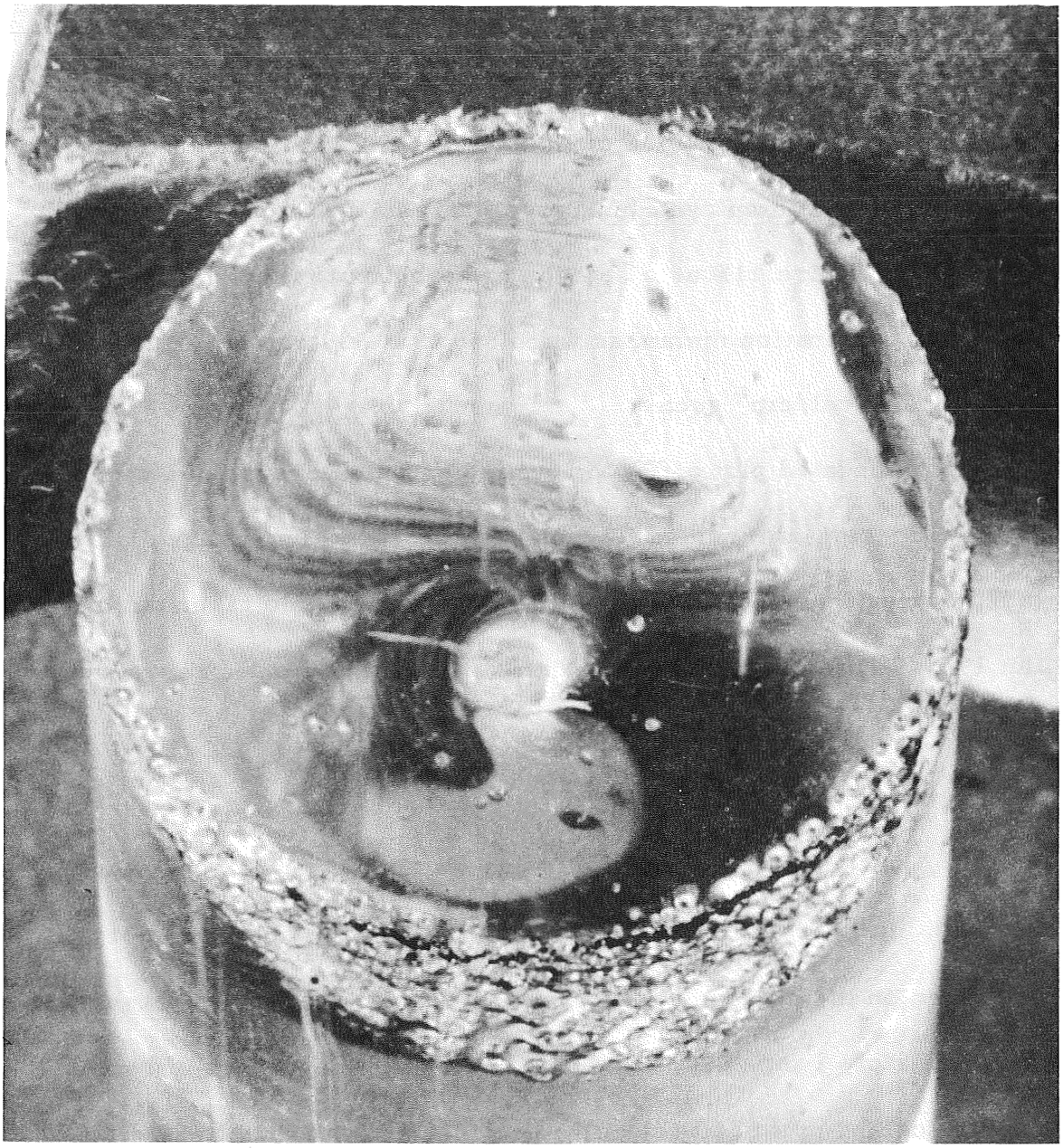

Figure 10. Face of PMM sample exposed to 500 cal/cm^2 sec. Indentation made by blunt probe is directly above center of circular face.

have observed the existence of liquid layers at lower surface regression rates[2, 5]--they indicated that transition to liquid-like behavior occurs at about 600°K. Using this as an arbitrary definition, it is possible to obtain a measure of liquid layer thickness from the subject data. These are displayed in Figure 11A as a function of regression rate and in Figure 11B as a surface of heat flux to the surface. The blunt rod penetration distances were 850 μ at 500 cal/cm^2 sec and 220 μ at 150 cal/cm^2 sec.

An updated plot of PMM regression rate versus cold-wall thermal loading is included for completeness as Figure 12. Data taken during the 1967-68 program is plotted with data taken during the 1968-69 program. The rate data appears to be quite reproducible even though sample PPM specimens were from completely different vendor batches.

A set of ICRPG propellant runs was made in the arc-imaging furnace. In all cases the sample was ignited by the optical energy deposited on the surface. The observed burning rate in all cases was approximately 1 mm/sec, and appeared to be independent of radiant energy loading up to 200 cal cm^{-2} sec^{-1} --the maximum tested.

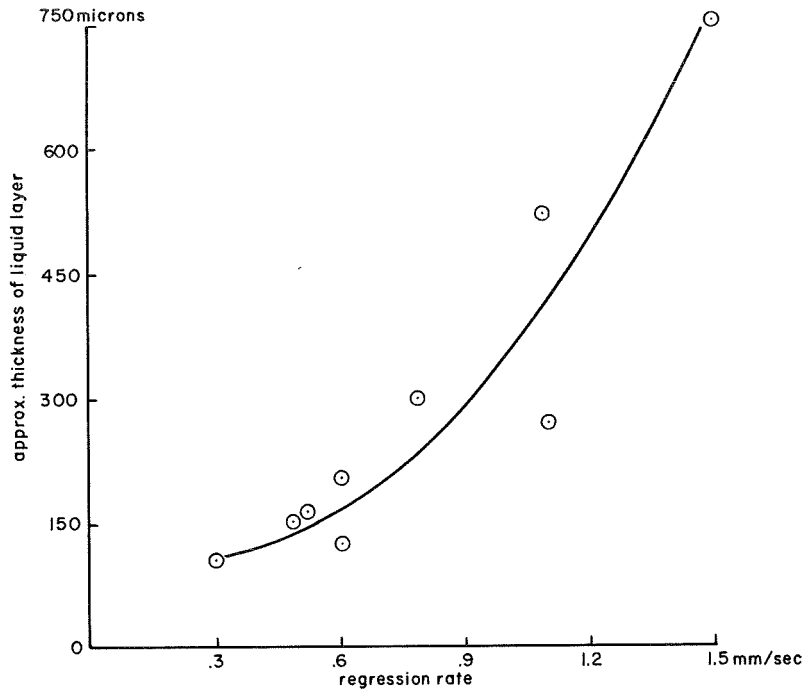

Figure 11A. Thickness of liquid layer in PMM vs regression rate.

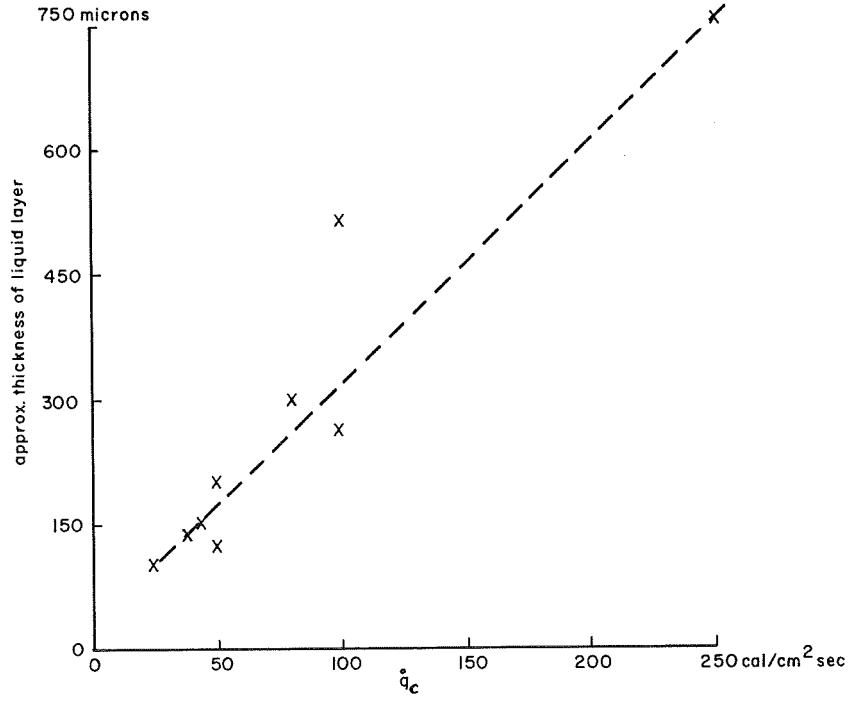

Figure 11B. Thickness of liquid layer in PMM vs cold-wall thermal loading, $\dot{q}_c$.

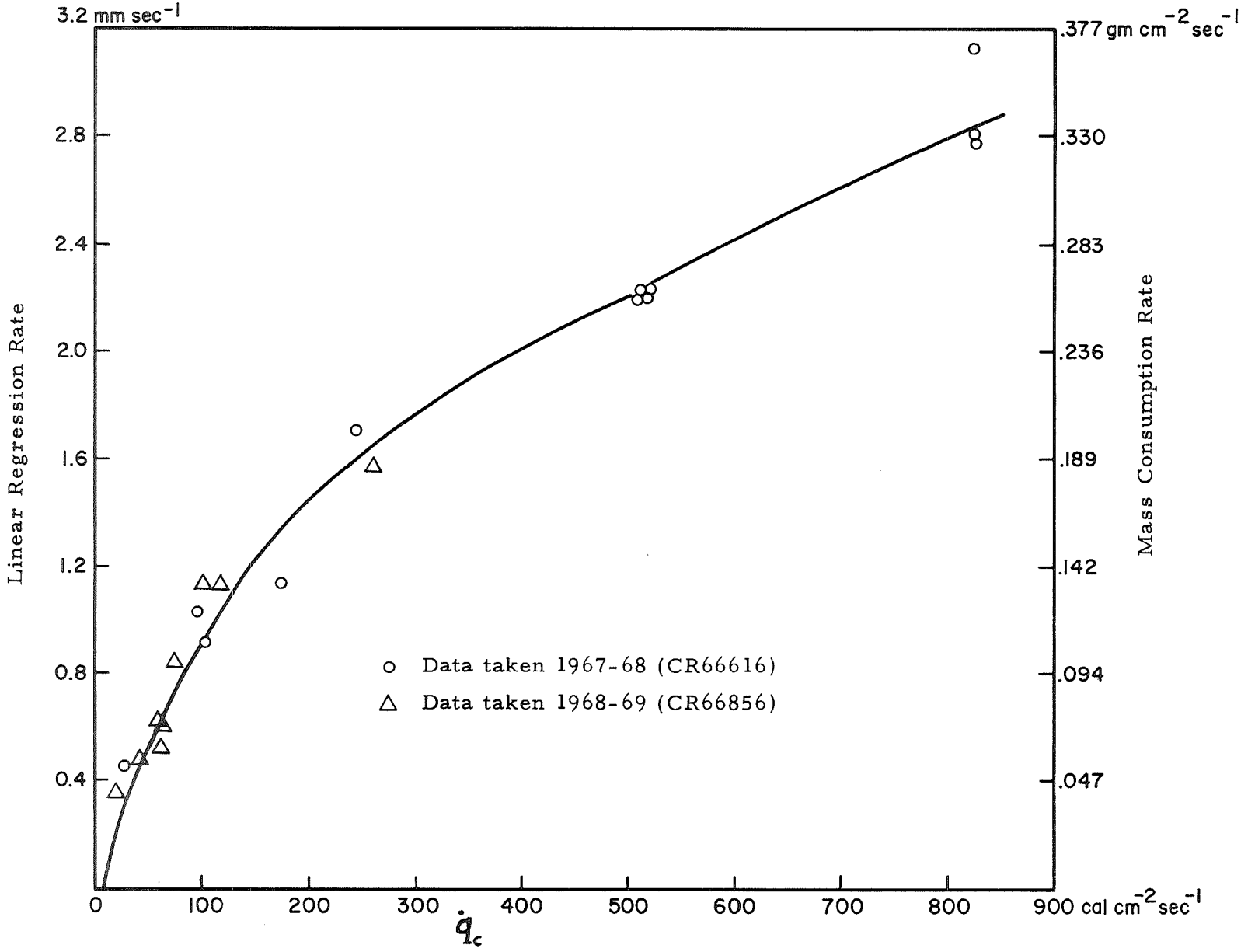

Figure 12. Regression rate vs cold-wall thermal loading, $\dot{q}_c$, for PMM.

IV. DISCUSSION OF RESULTS

Development of the novel temperature measuring technique occupied so much of the subject program that insufficient time was available to take the amount of data required for a clear interpretation of the underlying mechanism of PMM linear pyrolysis. However, a major finding that does have impact on the role of the binder in the composite propellant deflagration process is the extent of the liquid layer.

The evidence for its existence--temperature distribution, visual observation, and penetration of objects thrust into the surface--is very strong indeed. And although its existence was not considered by early workers[3], it was noted by later workers[2] and has been reported very recently to be pervasive in a number of polymeric materials[5].

The dependence of liquid layer depth on surface heating exposure at low regression rates, say below 0.3 mm/sec has been reported to be opposite[2] that found by the author (Figure 11A). Assuming that both sets of data are correct, this suggests that a change occurs at some intermediate condition. Figure 9 supports the possibility of a change at approximately 0.3 mm/sec.

A mechanism that is consistent with the observations is that:

(a) surface vaporization is the rate-limiting step.

(b) liquefaction of PMM occurs at about 600° K for the conditions of present interest, and has a high "activation energy" so as not to be rate-limiting.

(c) the liquid layer is turbulent.

Thus, an incremental increase of surface heat flux results in an increase of surface temperature and therefore surface regression rate (Figure 8). The turbulence in the liquid layer "smooths out" the thermal gradient, although the resulting influence on the liquefaction rate is relatively large (high activation energy), so more liquid is produced until a new equilibrium is reached.

The presence of the turbulent liquid layer precludes interpretation by techniques that assume diffusional transport[2, 3]. But on the other hand, the lack of strong subsurface gradients permits interpretation of the surface vaporization process on kinetics grounds, uncluttered by the influence of gradients. Thus, Figure 9 suggests the "activation energy" for the liquid-vapor conversion of PMM is $38\ ^{+2}_{-17}$ kcal/mole. Although values for bulk degradation of PMM at low temperature are given in the literature (Reference 3) as lying between 30 and 40 $\frac{\text{kcal}}{\text{mole}}$, the apparent agreement is probably fortuitous.

The presence of a liquid layer on the surface of a burning polymer could strongly influence its overall combustion characteristics. For example, it appears to be the principal cause for the "anomalous" behavior of the ICRPG standard reference propellant and other composite solid propellants of practical interest[6].

V. REFERENCES

(1) Simon, D. R. and McAlevy, R. F. III, "Rapid Pyrolysis of Composite Solid Propellant Ingredients," NASA CR-66616, June 1968.

(2) McAlevy, R. F. III, Lee, S. Y. and Smith, W. H., "The Linear Pyrolysis of Polymethylmethacrylate During Combustion," AIAA Journal, Vol. 6, No. 6, pp. 1137-1142 (1968).

(3) Chaiken, R. F., Anderson, W. H., Borsh, M. K., Mishuck, E., Moe, G. and Schultz, R. D., "Kinetics of the Surface Degradation of Polymethylmethacrylate," J. Chem. Phys., Vol. 32, No. 1, pp. 141-146 (1960).

(4) Kantrowitz, A. R., Camac, M., Litvak, M. M., Patrick, R. M., Petcheck, H. E., Plasma Physics and Controlled Nuclear Fusion Research Conference Proceedings, Salzburg, Austria, 4-9 September 1961, 1962 Supplement - Part 2.

(5) Havel, J. V., "The Linear Pyrolysis of Several Thermoplastics During Combustion," 1969 Master's Thesis, Stevens Institute of Technology.

(6) Private Communication, R. F. McAlevy III, July 17, 1970.